

THE DETERMINATION OF MAGNESIUM

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THE DETERMINATION OF MAGNESIUM

Magnesium is abundant and widespread, particularly in the soils and rocks of Southern Ontario where it occurs mainly with calcium, but in smaller quantities. It thus occurs in concentrations second only to calcium in our waters, generally making up from one-quarter to one-half of the hardness.

Magnesium is essential to both plants and animals. It is non-toxic, but particularly in non-acclimatized individuals, may produce a cathartic effect at levels greater than 125 mg/l, a concentration well above those usually found in either our surface or ground waters.

1. Sample Handling and Preservation

Glass or polyethylene bottles are acceptable for sample collection. No preservation is required for surface or ground water samples. For industrial waste samples analyzed by atomic absorption, see *Determination of Trace Metals*.

2. Selection of Method

Three approaches are used for the determination of magnesium in surface and ground waters. Method A calculates magnesium values from the difference between the total and calcium hardness results and is usually applied to drinking water samples. It is described only in summary. Method B an automated analyses by atomic absorption spectrophotometry (AAS), is used routinely for surface waters. The method described in *Determination of Trace Metals* is used on industrial wastes and in the regional laboratories.

MAGNESIUM
CALCULATION METHOD A

SUMMARY

Substance determined.	Mathematical difference between total and calcium hardness reported as <i>mg/l Mg</i> .
Interpretation of results.	The magnesium value is obtained by subtracting a calcium measurement from a hardness measurement using the appropriate conversion factors. If the major hardness producing ions present in the sample are calcium and magnesium then this calculated value closely approximates the actual magnesium content. If however, other hardness producing metallic ions are present (i.e. iron, aluminum, manganese etc.) and are titrated as hardness, then the calculated magnesium will not approximate the actual value in the sample.
Principle of method.	A magnesium value is obtained by calculation: (Total hardness as CaCO_3 - calcium hardness as CaCO_3) $\times 0.243$ = magnesium as Mg^{++} . The total hardness is obtained by titration with EDTA (see <i>Determination of Hardness</i>) and the calcium hardness can be obtained by either titration by EDTA (see <i>Determination of Calcium Method A</i>) multiplied by the appropriate factor or by atomic absorption spectrophotometry (see <i>Determination of Calcium Method B</i>) and (<i>Determination of Trace Metals</i>), multiplied by the appropriate factor. The normal method for obtaining the calcium value for this procedure is by EDTA titration.
Time required for analysis.	As many as <i>sixty</i> magnesium results could be calculated, in a batch, in <i>one hour</i> .
Range of application.	Dependant on methods used for hardness and calcium analysis usually 2 to 300 <i>mg/l</i> . Higher levels can also be calculated.
Standard deviation.	Dependant on methods used for hardness and calcium analysis usually ± 3 <i>mg/l</i> .
Accuracy.	Dependant on methods used for hardness and calcium analysis usually $\pm 1\%$.

SUMMARY

Limit of detection.	Dependant on methods used for hardness and calcium analysis usually 2 mg/l.
Interferences and shortcomings.	For sewage and industrial waste samples the presence of divalent metals, other than calcium and magnesium, can contribute to the measured total hardness, which in turn will affect the concentration of the magnesium result reported.
Minimum volume of sample.	None, other than the amounts required for the total and calcium hardness.

MAGNESIUM

AUTOMATED ATOMIC ABSORPTION - METHOD B

SUMMARY

Substance determined.	Magnesium ion Mg^{++} .
Interpretation of results.	Results are reported as mg/l Mg .
Principle of method.	An automated atomic absorption method is used to measure the concentration of magnesium ions. The sample is diluted with a releasing agent, lanthanum chloride, prior to aspiration into the burner flame.
Time required for analysis.	About 200 samples may be analyzed in one day.
Range of application.	Working ranges are: $0 - 6.0$ mg/l Mg $0 - 30$ mg/l Mg
Standard deviation.	± 0.04 for the range $0 - 6$ mg/l ± 0.40 for the range $0 - 30$ mg/l
Accuracy.	Within precision of method.
Limit of detection.	.128 mg/l Mg .
Interferences and shortcomings.	Metals such as sodium, potassium, and calcium cause no interference at concentrations less than 400 mg/l . Aluminum, silicates and carbonates tend to depress the absorbance if present in significant quantities. These interferences are controlled by addition of lanthanum chloride to the sample prior to aspiration.
Minimum volume of sample.	50 mls .
Preservation and sample container.	Glass or polyethylene bottles are acceptable for surface and ground water samples. For industrial waste samples see: <i>Determination of Trace Metals</i> .

SUMMARY

Safety considerations.

The possibility of burner flash-back or explosion is always present when using flame atomic absorption apparatus. The manufacturer's instructions for burner ignition, use and shut-down should always be rigorously followed, and the waste trap filled with water at all times. Standard safety procedures should be employed when working with compressed gas cylinders. Caution should be exercised during the preparation of the lanthanum chloride since concentrated acid is used.

MAGNESIUM

AUTOMATED ATOMIC ABSORPTION - METHOD B

1. Introduction

The sample under test, automatically mixed with a releasing agent, lanthanum chloride, is aspirated as a fine mist into the air-acetylene flame of an atomic absorption spectrophotometer. Light emitted from a hollow cathode lamp at a characteristic wavelength for magnesium, is directed through the flame into a monochromator and onto a detector. Magnesium atoms, heated in the flame absorb this light and the detector measures the decreased intensity of the resulting beam. The amount of light absorbed is directly proportional to the concentration of magnesium in the sample, and is recorded on a strip-chart recorder as a series of peaks, then compared to a calibration curve derived from simultaneously tested standards. The calibration curve is linear throughout the working range.

2. Interferences and Shortcomings

In the AAS method for magnesium there are few significant interferences from the concentrations of substances encountered in natural waters. Aluminum, silicates and carbonates, if present in substantial quantities, tend to depress the absorbance of magnesium. These interferences are controlled by the addition of lanthanum chloride to the sample prior to aspiration into the flame.

Partial clogging of the burner nebulizer and consequent reduction in aspiration rates may result from processing samples containing large amounts of suspended solids; pre-filtration of samples is advisable in such cases.

3. Apparatus

- a) Unicam SP 1900 Double Beam Atomic Absorption Spectrophotometer, located under an exhaust canopy.
- b) Corning double pen recorder Model #845 or equivalent.
- c) Gilson sample changer, Model #TDI ST/SCI 5 with 200 positions.
- d) Gilson Minipulse II pump, Model #HP 8.
- e) Manifolds as outlined in Figures I and II.

- f) Test tubes 17 mm X 150 mm (400).
- g) Test tube racks for above tubes (8).
- h) Air and acetylene, suitable for atomic absorption analyses.
- i) Stabiline Automatic Voltage Regulator, Type IES 9101B, Superior Electric Co.

*THE BURNER HEAD SHOULD BE CLEANED FREQUENTLY WITH
DETERGENT AND RINSED THOROUGHLY WITH DISTILLED WATER.*

4. Reagents

- a) Lanthanum oxide, La_2O_3 , reagent grade powder.
- b) Hydrochloric acid, HCl , concentrated, Aristar grade.
- c) Magnesium metal, reagent grade ribbon, high purity.
- d) Combined Stock Standard Solution

For the determination of sodium, potassium, calcium, and magnesium by atomic absorption spectrophotometry, a combined stock standard solution is prepared with the following concentrations:

Calcium	2000 mg/l Ca
Magnesium	600 mg/l Mg
Sodium	1000 mg/l Na
Potassium	600 mg/l K

Refer to the individual method write-ups for the preparation of each stock solution.

e) Stock Standard Magnesium Solution

Place 1.200 g of freshly cleaned metal ribbon into a 250 ml Erlenmeyer flask and carefully add 50 ml of 1:1 v/v hydrochloric acid in small quantities. Swirl contents of flask periodically. When dissolution is complete, transfer the contents of the Erlenmeyer flask to a 2000 ml volumetric flask, rinse the Erlenmeyer flask several times with deionized distilled water each time adding the rinses to the volumetric flask. Add each of the stock portions prepared for calcium, sodium and potassium to the contents of this 2000 ml volumetric flask and dilute to the mark with deionized distilled water. Thoroughly mix the solution and transfer to a plastic reagent bottle.

f) Working Standard Solutions

Daily calibration standards are prepared for each range as required by diluting the following aliquots to 1000 ml.

High Range

Combined Stock Standard Solution ml	50.0	40.0	30.0	20.0	10.0	5.0
Working Standards mg/l Mg	30.	24.	18.	12.	6.0	3.0

Prepare an intermediate standard solution by diluting 200 ml of Combined Stock Standard Solution to 1000 ml (120 mg/l Mg).

Low Range

Intermediate Standard Solution ml	50.0	40.0	30.0	20.0	10.0	5.0
Working Standards mg/l Mg	6.0	4.8	3.6	2.4	1.2	0.60

g) Lanthanum Chloride Solution

Dissolve 8.00 g La_2O_3 in 200 ml deionized distilled water containing 20 ml concentrated hydrochloric acid. When dissolution of the salt is complete, dilute the solution to 4000 ml using deionized distilled water and mix thoroughly. The pH of this solution should be approximately 1.7. Store the solution in a plastic bottle.

High and Low Range Magnesium

For both ranges, 2.00 ml of LaCl_3 is proportioned with sample yielding a lanthanum concentration of approximately 1380 mg/l at the burner head.

h) Quality Control Samples

Prepare Quality Control A and B solutions QC-A and QC-B respectively, that will provide test solution for at least twenty days of analysis. The concentration of the QC-A and QC-B should be chosen such that they fall within the normal concentration range of samples being routinely analyzed. These quality control checks are used to detect systematic error such as blank or calibration changes from day to day and must be included in each run of standards and samples on a day to day basis. When preparing new QC-A and QC-B solutions, do so early and monitor their response in comparison with the old set for at least *three days* prior to adopting them.

5. Procedure

The danger of burner flash-back and/or explosion is always present while using flame atomic absorption apparatus. The manufacturer's procedures should be carefully followed for ignition, use, and shut-down of the burner. Normal safety precautions must be exercised when transporting and using compressed gas cylinders.

THE AAS UNIT MUST NOT BE LEFT UNATTENDED WHILE IT IS IN OPERATION.

The analytical procedure for magnesium is identical to that described under the *Determination of Calcium* with the following exceptions:

wavelength 285.2 nm (magnesium lamp)

6. Calculation and Reporting

The peak heights are converted directly to concentrations units, mg/l Mg by a calibration curve or by the Hewlett Packard digitizer. Results are reported as follows:

<u>Range</u>	<u>Report to</u>
0 - 6 mg/l Mg	2 significant figures
0 - 30 mg/l Mg	2 significant figures

7. Precision and Accuracy

Standard Deviation in mg/l	Duplicates	Range mg/l Mg
±0.04	Within-run	0 - 6
±0.40	Within-run	0 - 30

8. Bibliography

- i) Standard Methods for the Examination of Water and Wastewater, 13th ed., APHA Washington, D.C., 1971.*
- ii) Users Manual, Unicam SP 1900 Series Atomic Absorption Spectrophotometers. Pye Unicam Ltd. Cambridge England, Publication No. 299408.*
- iii) Outlines of Analytical Methods, Ontario Ministry of the Environment, Laboratory Services Branch, February 25, 1975.*

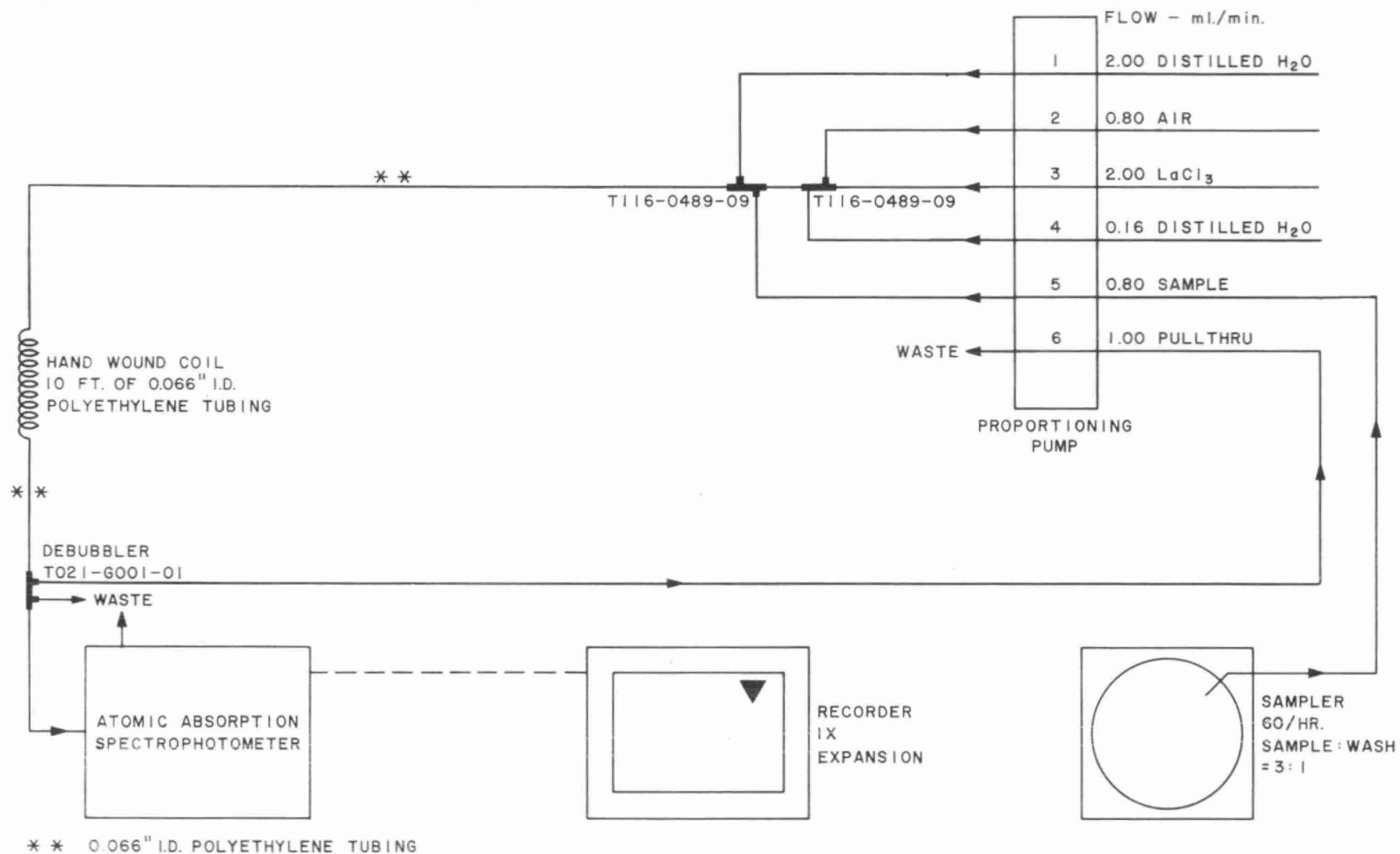


FIGURE I - ATOMIC ABSORPTION MANIFOLD FOR MAGNESIUM - METHOD 'B'
RANGE: 0-6 mg/l

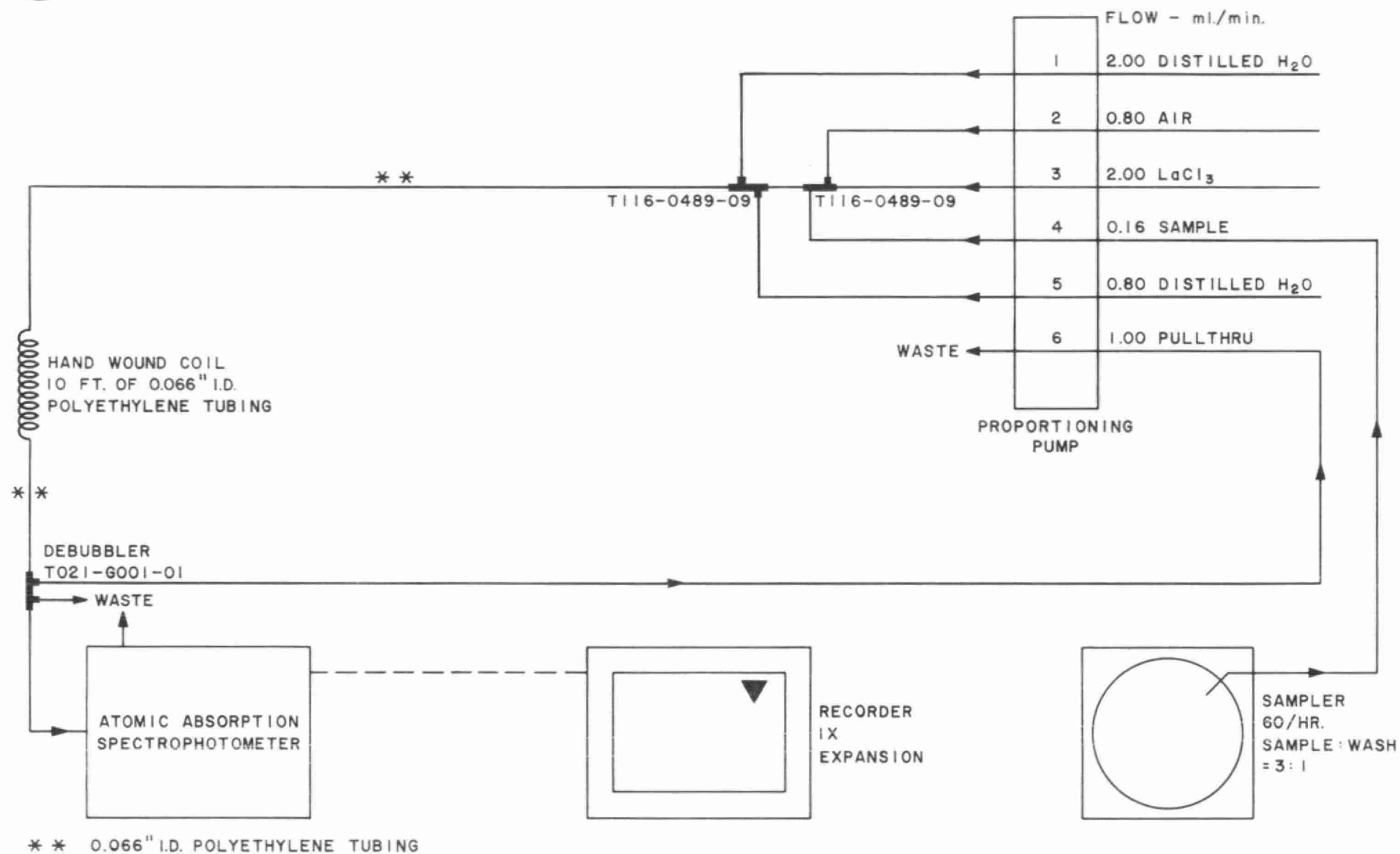


FIGURE II - ATOMIC ABSORPTION MANIFOLD FOR MAGNESIUM - METHOD 'B'
RANGE: 0-30 mg / l



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